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(54) Title: INCORPORATION OF HARD PARTICLES IN AN ELASTOMERIC MATRIX

(57) Abstract

A new use of hard particles to be incorporated in an elastomeric matrix to stop the onset of tears, cuts or perforations even in the presence of intense external stresses. The particles have a grit selection comprised between F8 and F220 and preferably between F12 and F80 according to FEPA standards. The percentage by volume of said particles with respect to the total volume of said elastomeric matrix plus said particles is comprised between 3 % and 50 % and preferably between 8 % and 30 %.

INCORPORATION OF HARD PARTICLES IN AN ELASTOMERIC MATRIX

The present invention relates to a new use of hard particles to be incorporated in an elastomeric matrix.

As is known, elastomeric mixes are currently used to manufacture a very large number of products, such as for example solid or pneumatic rubber tires, shoe soles. bearings, conveyor belts, etc.

Very often, product constituted by such elastomeric mixes are subjected to intense stress due to their use, as occurs for example with heavy-duty conveyor belts or tires for vehicles working in quarries or mines or in ironworks, steelworks, glassworks, pig-iron foundries, etc., which cause tears, perforations or cuts in the elastomeric mix, with the consequent breakdown of the entire mix and rejection of the item made of this mix.

This therefore leads to very high costs due to the need to discard the product that has become unusable due to the tears, perforations and cuts to which it has been subjected during its above described heavy-duty use, and due to the consequent machine and plant downtimes.

Patent US 3,850,875 and patent application PCT WO 89/06670 teach the use of a composition that contains hard particles incorporated in an elastomeric matrix merely to obtain an antiskid effect, particularly for tires.

In this situation, the technical aim of the present invention is to find a new use for hard particles to be incorporated in an elastomeric matrix.

In particular, the present invention relates to a new use of hard particles to be incorporated in an elastomeric matrix to stop the onset of tears, cuts or perforations even in the presence of intense external stresses.

It is observed in practice that these external stresses can be even higher than the internal cohesion forces of the elastomeric mix.

This solution allows to stop, within the mix, the spread of tears caused also, for example, by tangential shear, traction, compression and flexural stresses to which the item is subjected especially in heavy-duty uses.

Preferably, these particles have a grit selection between F8 and F220 and preferably between F12 and F80 according to the prescriptions of FEPA Standard 42-GB-1984, Test sieves: ISO 565-1983.

Preferably, the volume percentage of these particles with respect to the total volume of the elastomeric matrix plus the particles is between 3 and 50% and preferably between 8 and 30%.

Preferably, these particles have a substantially round

average shape.

Preferably, these particles are made of a material which has a hardness greater than 3, preferably greater than 6.5, more preferably greater than 7.5 in the Moh's scale.

Preferably, the elastomeric matrix has a hardness between 40 Shore A and 100 Shore A and preferably between 55 Shore A and 85 Shore A.

The composition that contains the hard particles incorporated in an elastomeric matrix usable according to the present invention can be obtained by means of a process which consists in fully covering the surface of a preset amount of hard particles with at least one layer of a product that has high adhesive or cover-coating characteristics, when adequately heated, both with respect to the mix and with respect to the hard particles; in uniformly mixing the coated particles together with the as yet not cured elastomeric mix; in curing the mix thus obtained at a preset temperature and for a preset time to achieve the complete curing of the adhesive or cover-coat with the mix and simultaneously with the particles.

The process for preparing the composition is performed by means of the following succession of steps.

First of all, a preset amount of particles made of hard material, such as metal, ceramic, synthetic organic materials, preferably having no edges or corners where

maximum stresses would concentrate, is taken.

Then the surface of each particle is coated with one or more layers of a product that has high adhesive or cover-coating characteristics, when adequately heated, both with respect to the elastomeric mix in which the particle is to be subsequently incorporated and with respect to the particle itself.

The hard particles, coated with at least one layer of adhesive or cover-coat, are then uniformly mixed together with the as yet not cured elastomeric mix.

The elastomeric mix that contains the particles is cured at such a preset temperature and for such a preset time as to allow full and perfect curing of the layer of adhesive with the mix and with the particles simultaneously.

By virtue of the curing of the adhesive or cover-coat, one obtains a product that has no discontinuities and in which the characteristics of the cured mix remain unchanged except for a plurality of regions, uniformly distributed inside it, where the particles are accommodated; these regions have increased physical resistance characteristics mainly as regards tearing.

The advantage of using particles that have a round and continuous -- and thus substantially spherical -- surface allows to distribute the stresses that occur on each particle uniformly per surface unit.

In other words, it is possible to spread these stresses on the entire interface between the particle and the elastomeric mix, containing them below the cohesion force of the material.

In addition to coating with at least one layer of adhesive product, each particle can also be coated with at least one second layer of a crude elastomeric mix which is substantially harder than the mix in which the particle is to be incorporated, so as to better distribute the energy, generated by low- or medium-frequency stresses, to which the finished product is subjected during use.

In this manner it is furthermore possible to considerably reduce shearing stress at the interface, i.e. at the surface of contact between the particle and the elastomeric mix, thus inhibiting the forming or onset of tears, cuts or the like.

As an alternative to the second layer of the second crude elastomeric mix, or in addition to it, each particle can have, below the layer of adhesive or cover-coat, at least one layer of primer to enhance adhesion between the particle and the adhesive.

In order to improve perfect adhesion and contact between the particles and the mix it is possible to use adhesion promoters placed between the interfaces of the various covering layers of the particle or incorporated directly in

the adhesive, in the primer, in the crude elastomeric mix, etc. These adhesion promoters can be pyrogenic silica, titanates and silanes.

For example, the addition of pyrogenic silica also reduces, by virtue of a thixotropic effect, the tendency of the dry surface of the adhesive coating of the particle to "dust" when crude, especially in some kinds of coating, such as for example adhesive products in aqueous suspension.

The particles thus coated with one or more layers preferably have a substantially spheroidal shape, so that during their preparation they tend to agglomerate much less than sharp-edged particles, which would have smooth faces that adhere to each other.

This lower tendency to agglomerate furthermore allows, as mentioned, to coat the particles with hard crude rubber above the layer of adhesive.

The particles can furthermore be surface-treated before being coated with one or more layers.

Possible surface treatments are, for example, oxidation or chemical washing, for example with hydrofluoric acid. The elastomeric mixes with high resistance to perforation and tearing obtained with the above described process thus have a plurality of hard particles uniformly distributed inside them and coated with at least one layer of material with high adhesive properties that has undergone curing with the

mix s during their curing.

Each one of these particles, according to the requirements, can furthermore have, over the layer of adhesive, at least one layer of a crude elastomeric mix (substantially harder than the mix in which the particle is incorporated) that considerably reduces shearing stress and the moment of flexure at the interface.

As an alternative, or in addition, to the layer of crude elastomeric mix, each particle can have at least one layer of primer beneath the layer or layers of adhesive, and adhesion promoters between or within these layers.

The elastomeric mix may furthermore have, inside it, particles having different particle sizes in order to form an internal barrier against tearing and simultaneously against perforation of the finished product, which may be for example a tire.

In fact, if the elastomeric mix obtained with the above process forms a solid or pneumatic tire, this tire can have, for example, at least one anti-perforation and anti-tear layer arranged inside it and on the sidewalls of the solid or pneumatic tire.

If the hard particles have chemically and physically inert surfaces, (for example in the case of silicon carbide, boron nitride, etc.), before performing the above described process it is possible to pre-coat the particles to improve

adhesion of the adhesive to the particle on which it is applied.

Particularly, the pre-coating of the particles consists in coating them with a ceramic adhesive, such as an alkaline silicate.

As an alternative to ceramic adhesive it is possible to use an epoxy resin at temperatures below 100 degrees, whereas a ceramic glass can be used in hot conditions (above 600 degrees).

The particles are subsequently coated with a powdered product to achieve surface roughness and are kept in motion during this step for example in a tumbling barrel or in a fluid bed until they have dried partially.

Corundum, quartz, ground porcelain, alumina, etc. can be used as a powered product.

Finally, the particles are heated to a temperature that is higher than the melting temperature of the ceramic adhesive, so that the powdered product adheres perfectly and permanently on each one of the hard particles during the subsequent cooling step.

Once this pre-coating step has been completed, the process already described is performed.

The invention thus achieves the intended aim and achieves

numerous and important advantages.

The invention will become apparent with reference to the outcomes of the tests enclosed by way of non-limitative example, illustrated with reference to the accompanying figures, wherein:

Figure 1 is a photograph that illustrates use according to the invention;

Figure 2 is a photograph that illustrates the use according to Figure 1, wherein the tire has been washed;

Figure 3 is a reduced-scale photograph that illustrates the use according to Figure 1;

Figures 4 to 6 are photographs that illustrate the prior art for comparison purposes;

Figure 7 is a schematic view of the test device;

Figure 8 is an enlarged-scale perspective view of the device of Figure 7.

In all the tests, the elastomeric matrix has the following composition:

-- Type SMR 10 natural rubber (Standard Malaysian Rubber 10é	PHR 60
-- SBR 1712 oil extended SBR 1712é (Styrene Butadiene Rubber 37.5 phr aromatic oil)	PHR 55

-- Carbon Black N234 or N220 (N = normal curing)	PHR 60
-- Aromatic oil	PHR 10
-- Zinc oxide	PHR 5
-- Stearic acid	PHR 1.5
IPPD (Antiflex cracking agent)	
(isopropyl-phenyl-paraphenylene-diamine)	PHR 1.0
-- Electol H or ANOXHB or Vulkanox HS (Polymerized 2,2,4 trimethol 1,2 dihydroquinoline)	PHR 10
-- Poliplastol 6^{o} (Processing aid. Fatty ester based)	PHR 3.0
-- RIOWAX 721 or ANTILUX 654 (paraffin wax)	PHR 1.0
-- Koresin (tacky fier)	PHR 3.0
-- 1% oil treated sulfur	PHR 2.0
-- CBS (cyclohexyl-2-benzothiazyl-sulphenamide)	PHR 1.0

In all the tests, the hard particles are prepared by coating them, using a spray method, with a primer that has the following composition:

-- Carbon tetrachloride	0.1%
-- Formaldehyde	1.0%
-- Ethylbenzene	3.0%
-- Titanium dioxide	5.0%
-- Xylene	15.0%
-- Methyl isobutyl ketone	60.0%
-- Methyl ethyl ketone	2.0%
-- Phenolic resin based on phenol derivatives and methylene donors (thermosetting)	13.9%

The hard particles are then heated to a temperature of about 50 °C to accelerate the process without curing the primer, and cooled, thus obtaining a final primer thickness of approximately 4-10 microns, and are covered, by means of a spray method, with a cover-coat that has the following composition:

-- 2,5-dinitrosoparacymene	50 parts
-- Soluble, fusible, acid-catalyzed phenol-formaldehyde resin	50 parts
-- Hexamethylenetetraamine	4.0 parts
-- Methanol	65.0 parts
-- Methyl ethyl ketone	60.0 parts

After cooling, the particles have a final cover-coat thickness of 10-15 microns.

The particles are then cold-mixed with the matrix in an open mixer and the composition is then cured in a still mold according to the known art.

All tests are carried out at room temperature and in dry conditions if not otherwise specified.

The specified grit selection refers to the above mentioned Fepa standards.

TEAR TESTS

-- Scope of the tear tests

The scope of the tear tests is to duplicate in the laboratory the tear suffered by rubber goods with and without anti-tear particles in order to evaluate the improvement attained with the addition of the particles to the rubber.

A) The Rotating Cylinder Tear Test duplicates the tearing effect of sharp metal scrap falling on conveyor belts, rubber-lined ball, rubber-lined silos, rubber-lined dumpers, rubber-lined ball-and-rod mills and the like.

-- General notes:

The test consists in placing in a horizontal cylinder, with an inside diameter of 1.1 m, a depth of 0.4 m, with six 100x400 internal horizontal blades fixed to the cylinder:

- 10 test pieces
- 100 kg of sharp metal tearing particles of which at least 30 kg in pieces of not less than 5 kg each.

The cylinder rotates about its horizontal axis at 10 rpm for 1 hour.

The test pieces have a parallelepiped shape, 100 mm x 200 mm x 30 mm. Three of the 10 pieces contain no hard particles and serve as reference.

-- Visual evaluation scale

At the end of the test run, the 10 test pieces are evaluated for:

Chipping (P), Chunking (C), Tearing (T),
according to the following scale:

1 = none
2 = very slight
3 = slight
4 = moderate
5 = accentuated
6 = very accentuated
7 = considerable
8 = severe
9 = heavy
10 = very heavy

The weight of the three test pieces without particles and the seven test pieces with particles is determined.

The results are given in tables 1 to 6.

TABLE 1

Quality of particles: spherical corundum (SKO)

Grit selection: F16

Test	1	2	3	4	5	6	7	8	9	10
% Weight reduction	32	30	26	10	8	10	8	8	9	10
Chipping = P	//	//	//	5	5	6	5	5	5	5
Chunking = C	7	8	7	3	5	3	3	3	3	3
Tearing = T	8	8	8	4	6	4	5	5	4	4
Particles % by volume	0	0	0	14	14	14	14	14	14	14

Remarks: In tests 1, 2 and 3, chunking and tearing were prevailing. Chipping is not noticeable.

TABLE 2

Quality of particles: spherical corundum (SKO)

Grit selection: F16

Test	1	2	3	4	5	6	7	8	9	10
% Weight reduction	38	40	32	8	6	8	8	6	8	8
Chipping = P	//	//	//	3	4	4	4	4	4	4
Chunking = C	9	9	9	4	3	5	4	3	3	3
Tearing = T	7	8	6	2	2	1	2	2	2	2
Particles % by volume	0	0	0	14	14	14	14	14	14	14

Remarks: Wet test: 5 liters of water were placed in the cylinder at the start. Water acts as lubricant for the tearing media of the 100 kg load.

TABLE 3

Quality of particles: spherical corundum (SKO)

Grit selection: F16

Test	1	2	3	4	5	6	7	8	9	10
% Weight reduction	26	27	30	15	20	18	16	16	16	16
Chipping = P	//	//	//	3	4	3	4	3	3	4
Chunking = C	8	8	8	4	5	5	4	4	4	4
Tearing = T	8	8	8	6	6	6	5	6	6	6
Particles % by volume	0	0	0	9	9	9	9	9	9	9

Remarks: Dry test. In tests 1, 2 and 3, chunking and tearing were prevailing. Chipping is not noticeable.

TABLE 4

Quality of particles: spherical corundum (SKO)

Grit selection: F16

Test	1	2	3	4	5	6	7	8	9	10
% Weight reduction	30	31	31	15	15	18	18	16	17	16
Chipping = P	//	//	//	5	5	4	4	5	4	4
Chunking = C	8	9	9	6	5	6	6	5	4	5
Tearing = T	7	7	7	7	6	6	6	6	6	7
Particles % by volume	0	0	0	9	9	9	9	9	9	9

Remarks: Wet test.

TABLE 5

Quality of particles: spherical corundum (SKO)

Grit selection: F80

Test	1	2	3	4	5	6	7	8	9	10
% Weight reduction	25	24	23	20	15	15	16	16	18	15
Chipping = P	//	//	//	4	4	4	3	2	3	3
Chunking = C	8	7	7	5	4	4	4	5	5	5
Tearing = T	8	7	7	5	5	4	5	5	5	5
Particles % by volume	0	0	0	9	9	9	9	9	9	9

Remarks. Dry test. In all tests without particles, no chipping, tearing and chunking are prevailing.

TABLE 6

Quality of particles: spherical corundum (SKO)

Grit selection: F80

Test	1	2	3	4	5	6	7	8	9	10
% Weight reduction	26	26	27	21	21	18	18	20	16	20
Chipping = P	//	//	//	4	5	4	5	4	4	4
Chunking = C	7	9	7	3	3	4	3	3	3	3
Tearing = T	8	9	8	6	5	4	4	5	5	5
Particles % by volume	0	0	0	9	9	9	9	9	9	9

Remarks: Wet test. In all tests without particles, no chipping, tearing and chunking are prevailing.

A) General remarks on rotating cylinder tests

All tests with hard particles incorporated in the rubber gave much better results than the reference test pieces without particles.

- "Chipping" is more accentuated with fine particles.
- "Chunking" is slighter with medium particles
- "Tearing" is more present with medium-large particles
- Wet tests accentuate the effect of tests by at least one point on account of the lubricating effect of water.

B) The roadwheel test duplicates the tearing effect of sharp metal scrap on the tread and sidewall of solid-rubber and pneumatic tires.

-- General notes

The test consists in running a given solid-rubber tire against a small roadwheel with a surface that duplicates a scrap-metal yard flooring.

Figures 7 and 8 illustrate the configuration of the test device, in which, in particular, a solid-rubber tire 10 has the dimensions 150/50-100 as per DIN 7845 or ETRTO, the shape KM 15 DG and the profile FL.

The freely pivoted tire 10 is supported by a lever 11 which is pivoted in 12 and loaded with a weight 13 so as to generate a thrust 15 on the drive wheel 14.

This thrust can be adjusted according to the weight 13.

With particular reference to Figure 8, the resting surface of the drive wheel 14 is formed by pieces of scrap metal welded to the surface of the drive wheel 14 itself.

The various test tires of the same group are all run at 250 rpm with four different loads (100 kg, 200 kg, 400 kg, 600 kg) and with five different percentages of the same grit selection. Each group concerns one grit selection: F12-F16-F24-F46-F80.

The test is terminated when the circumference or diameter is reduced by 20% or after 2 hours, whichever occurs first.

Results are indicated in terms of reduction percentage per minute.

Example: 1/120 mens that after 2 hours the diameter has become approximately 148-149.

TABLE 7

Grit selection: F12

Quality: COR (brown corundum)

% of grit by volume	0%	5%	10%	20%	30%
LOAD ON WHEEL					
100 kg	10/120'	12/120'	12/120'	14/120'	8/100'
200 kg	20/40'	20/90'	16/120'	17/120'	20/100'
400 kg	20/5'	20/25'	20/90'	20/95'	20/50'
600 kg	20/1'	20/20'	20/55'	20/55'	20/30'

Comments: All test with Grit perform better than the "no grit" comparison test.

No test with 600 kg load has reached 120'.

TABLE 8

Grit selection: F16

Quality: COR (brown corundum)

% of grit by volume	0%	5%	10%	20%	30%
LOAD ON WHEEL					
100 kg	14/120'	14/120'	16/120'	18/120'	10/85'
200 kg	20/40'	20/85'	20/100'	15/120'	15/120'
400 kg	20/1'	20/60'	20/90'	20/100'	20/65'
600 kg	20/1'	20/30'	20/60'	20/55'	20/55'

Comments: All test with grit perform better than the "no grit" comparison test.
No test with 600 kg load has reached 120 minutes.

TABLE 9

Grit selection: F24

Quality: COR (brown corundum)

% of grit by volume	0%	5%	10%	20%	30%
LOAD ON WHEEL					
100 kg	12/120'	14/120'	15/120'	20/90'	20/90'
200 kg	20/40'	20/10'	15/120'	15/120'	20/75'
400 kg	20/1'	20/90'	20/100'	20/100'	20/70'
600 kg	20/1'	20/30'	20/90'	20/85'	20/30'

Comments: All test with Grit perform better than the "no grit" comparison test.

No test with 600 kg load has reached 120'

TABLE 10

Grit selection: F46

Quality: COR (brown corundum)

% of grit by volume	0%	5%	10%	20%	30%
LOAD ON WHEEL					
100 kg	12/120'	14/120'	18/120'	18/120'	18/120'
200 kg	20/40'	20/90'	20/100'	18/120'	18/120'
400 kg	20/3'	20/80'	15/120'	15/120'	20/90'
600 kg	20/1'	20/45'	20/90'	20/90'	20/50'

Comments: All test with grit perform better than the "no grit" comparison test.

No test with 600 kg load has reached 120'

TABLE 11

Grit selection: F80

Quality: COR (brown corundum)

% of grit by volume	0%	5%	10%	20%	30%
LOAD ON WHEEL					
100 kg	12/120'	15/120'	20/120'	20/120'	20/95'
200 kg	20/35'	20/90'	20/100'	20/120'	18/120'
400 kg	20/1'	20/80'	18/120'	20/100'	20/80'
600 kg	20/1'	20/50'	20/100'	20/85'	20/65'

Comments: All test with grit perform better than the "no grit" comparison test.

The best percentages are 20% and 40% with loads above 200 kg. All 60% Grit tests are slightly inferior on account of excessive Grit percentage. No test with 600 kg load has reached the 120 minute maximum.

B) General remarks on roadwheel tests

All tests with hard particles in the rubber have given better results than the various "no grit" comparison rubber tires.

The coarse grit selections give moderate chunking, slight chipping and moderate tearing.

These values are referred to 200-kg and 400-kg loads. With a 600-k loads, these values increase by 1 or 2 points.

Fine grit selections resist tearing and chipping.

C) Quarry test

The purpose of the test is to observe in practice, in a quarry, the effectiveness of the use of hard particles according to the invention.

A lift truck used in a quarry was fitted with standard, conventional 300-15 solid-rubber tires for a four-month period.

The result is reported in Figures 4 to 6.

In particular, with reference to the above mentioned visual evaluation scale, Figure 4 illustrates a chunking equal to 9, Figure 5 illustrates a chipping equal to 7, a tearing equal to 7 and a chunking equal to 6, and Figure 6

illustrates a chipping equal to 3, a chunking equal to 10.

For four consecutive months, the same lift truck was fitted with tires formed with the above described composition for use according to the invention, particularly having hard particles of the following type:

Quality: spherical corundum Sko
Grit selection: F 14

Percentage by volume of the hard particles with respect to the total volume of the elastomeric matrix plus the volume of the particles: 15%

The result is reported in Figures 1 to 3.

In particular, with reference to the above mentioned visual evaluation scale, Figure 1 illustrates a chipping equal to 2, tearing equal to 1 and chunking equal to 1, Figure 2 is similar to Figure 1, except that the tire has been washed with water to allow better viewing of the result, and Figure 3 illustrates a lift truck at work in quarry.

The comparison clearly shows a dramatic and unpredictable improvement in the tear-resistance of the tire.

The invention thus conceived is susceptible to numerous modifications and variations, all of which are within the scope of the present inventive concept.

All the d tails may furthermore be replaced with technically equivalent elements.

CLAIMS

1. New use of hard particles to be incorporated in an elastomeric matrix to stop the onset of tears, cuts or perforations even in the presence of intense external stresses.

2. Use according to claim 1, wherein said particles have a grit selection between F8 and F220 and preferably between F12 and F80.

3. Use according to at least one of the preceding claims, wherein the percentage by volume of said particles with respect to the total volume of said elastomeric matrix plus said particles is between 3% and 50% and preferably between 8% and 30%.

4. Use according to at least one of the preceding claims, wherein said particles have a substantially round average shape.

5. Use according to at least one of the preceding claims, wherein said particles are formed with a material that has a hardness of more than 3, preferably more than 6.5 more preferably more than 7.5 in the Moh's scale.

6. Use according to at least one of the preceding claims, wherein said elastomeric matrix has a hardness between 40 Shore A and 100 Shore A and preferably between 55 Shore A and 85 Shore A.

7. Use according to at least one of the preceding claims, wherein said particles are chosen among: silicon carbide, boron nitride, corundum, quartz, ceramic material, alumina.

8. Use according to at least one of the preceding claims, wherein an elastomeric matrix containing hard particles is prepared with a process that consists in fully coating the surface of a preset amount of hard particles with at least one layer of a product that has high adhesive characteristics, when adequately heated, both with respect to said matrix and with respect to said hard particles; in uniformly mixing said particles thus coated together with said as yet not cured elastomeric matrix; and in curing said matrix thus obtained with said adhesive.

9. Use according to claim 8, wherein each one of said particles has, beneath said adhesive layer, at least one layer of a primer.

10. Use according to claim 8, wherein each one of said particles has, above said adhesive layer, at least one layer of a second crude elastomeric mix that is harder than said matrix.

11. Use according to at least one of claims 8 to 10, wherein said process comprises the use of adhesion promoters arranged between the interfaces of the various coating layers of said particles or inside said adhesive, said primer, and said second crude elastomeric mix.

12. Use according to at least one of claims 8 to 11, wherein said particles, before being coated, undergo a surface oxidation or chemical washing treatment.

13. Use according to at least one of claims 8 to 12, wherein said particles are treated with a ceramic adhesive prior to said coating and are subsequently treated with a powdered product suitable to adhere to said ceramic adhesive to achieve the surface roughening of said particles while keeping them under agitation until they have partially dried, said particles being heated to a temperature in excess of the melting temperature of said ceramic adhesive and subsequently cooled once they are thus coated.

14. Use according to every new characteristic or combination of characteristics described herein.

15. Solid or pneumatic tire having an anti-perforation and anti-tear layer formed by hard particles incorporated in an elastomeric matrix and arranged on the sidewalls of said solid or pneumatic tire.

Fig. 3

Fig. 1

Fig. 4

Fig. 2

Fig. 6

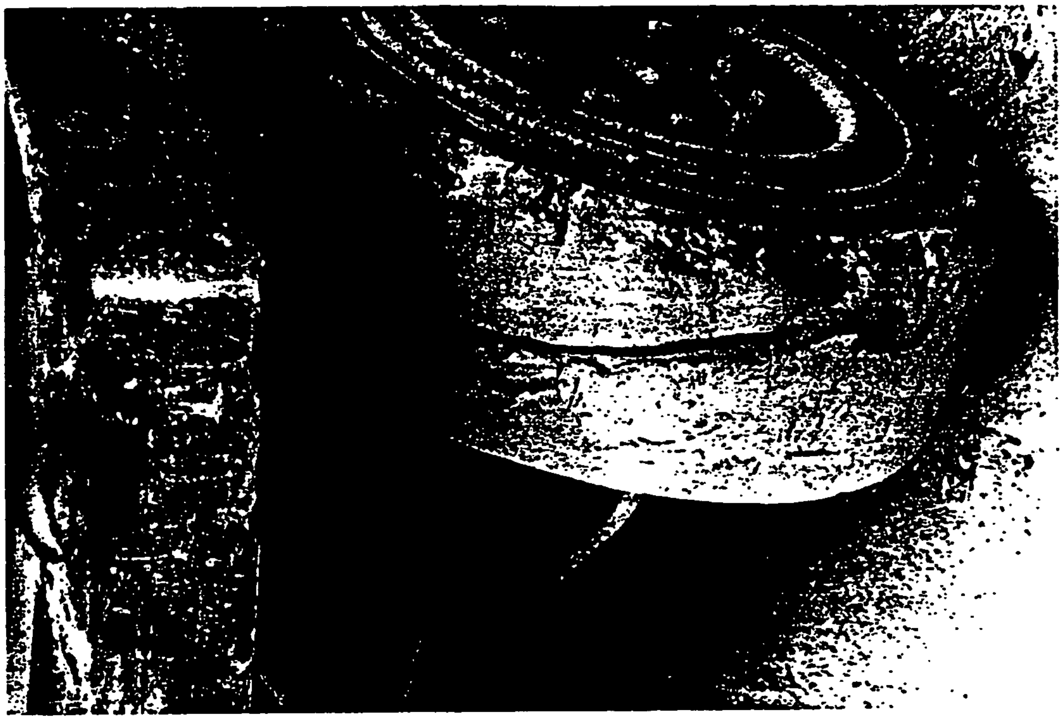

Fig. 5

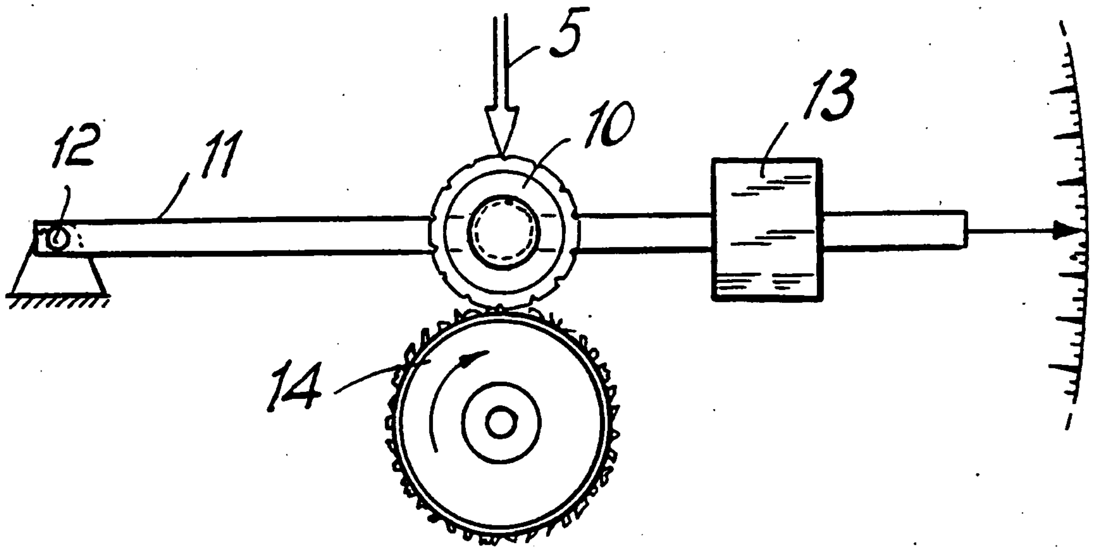

Fig.7

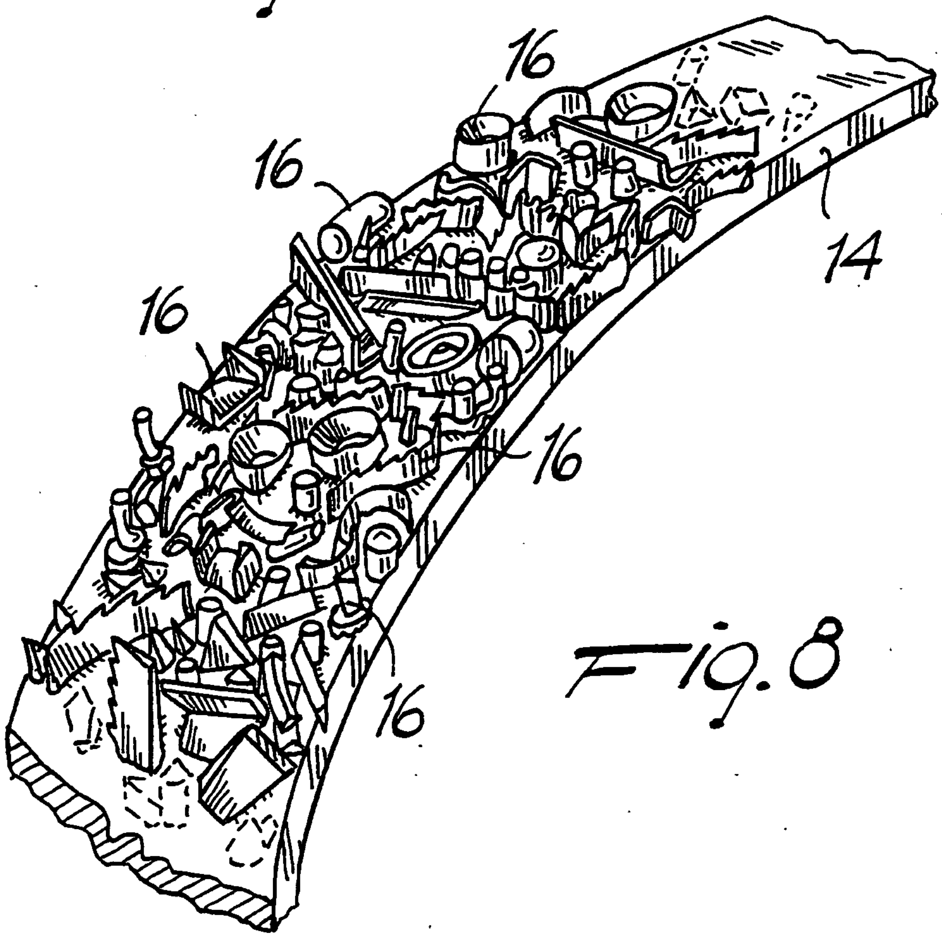

Fig.8

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08K3/00 C08K7/18 C08K9/10 B60C1/00 C08L21/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08K B60C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 461 469 (LONZA AG) 18 December 1991 see page 4, line 14 - line 20; claims ---	1-11,14
X	WO,A,89 06670 (KERATEK S.L.R.) 27 July 1989 cited in the application see claims ---	1-3, 5-11,14
X	FR,A,560 226 (R.OPPENHEIM) 1 October 1923 see page 1, column 2, line 51 - line 55; claims ---	1-7,14, 15
A	US,A,3 398 776 (E.B.REINBOLD) 27 August 1968 see column 2, line 11 - line 14 -----	15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
22 March 1994	11.04.94

Name and mailing address of the ISA	Authorized officer
European Patent ffice, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Humbeeck, F

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 93/03307

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0461469	18-12-91	CA-A-	2043663	01-12-91
		JP-A-	4227937	18-08-92
WO-A-8906670	27-07-89	EP-A-	0398914	28-11-90
		JP-T-	3504021	05-09-91
FR-A-560226		NONE		
US-A-3398776		NONE		